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Oxidation of Phenyl Radical by Copper(II) Complexes in Acetic Acid and in Acetonitrile[*1]

Keisuke WADA, Junzo YAMASHITA and Harukichi HASHIMOTO

Department of Synthetic Chemistry, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo

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The reactions between the phenyl radical and copper(II) complexes in acetic acid and in acetonitrile were investigated. It was found that the phenyl radical produced from the thermal decomposition of benzoyl peroxide in acetic acid is oxidized by the copper(II) ion to give a considerable amount of phenyl acetate. With cupric propionate, chloride, and bromide, "ligand-transfer" products, *i. e.,* phenyl propionate, chloro-, and bromobenzene, respectively, were also obtained. In addition, a larger yield of the oxidation product was obtained from a 1 : 1 complex than from a 1 : 3 complex of copper(II)-phenanthroline. These facts, together with the results on solvent effects, can be successfully explained on the basis of a ligand-transfer mechanism rather than an electron-transfer mechanism. The effects of substituents of benzoyl peroxide on the reaction were an electron-transfer mechanism. The effects of substituents of benzoyl peroxide on the reaction were so small that one cannot decide whether the ligand-transfer mechanism is a radical or an ionic one. Some abnormalities were observed in the reaction with cupric acetylacetonate. Additionally, the reaction with cuprous chloride was examined, and the behavior of the copper(I) ion in the reaction discussed.

It has long been known that organic free radicals can enter into oxidation-reduction reactions with transition metal ions.[1] Especially in the last half-decade, these reactions have attracted many chemists studying metal-promoted reactions.[2] To date, however, the information concerning these reactions has not been sufficient for their mechanisms to be fully confirmed.

The present investigation was undertaken as a part of a systematic study of the reaction mechanisms between organic radicals and transition metal complexes. In this report, the oxidation of the phenyl radical by copper(II) complexes will be discussed. The phenyl radical was produced from the thermal decomposition of benzoyl peroxide.

Experimental

Peroxides. The benzoyl peroxide was of a reagent grade. The bis-*p*-nitrobenzoyl peroxide and bis-*p*-methoxybenzoyl peroxide were prepared according to the method of Price and Krebs.[3] Table 1 lists the peroxides studied, together with other pertinent data.

Solvents. Reagent-grade acetic acid and acetonitrile were purified according to the methods of Vogel[4] and of O'Donnell and his co-workers[5] respectively.

Copper(II) Complexes. Anhydrous cupric acetate was prepared from its mono-hydrate by heating it at 130°C in a rotary evaporator for two days, recrystallizing it from dry acetone, and finally drying it *in vacuo* for three days. Cupric propionate mono-hydrate was prepared from equimolar amounts of sodium propionate and cupric sulfate in aqueous media. The anhydrous salt was prepared as in the case of cupric acetate. Anhydrous cupric chloride was prepared from commercial di-hydrate by heating it at 100°C for several days. The water in cupric bromide was removed by heating it at 105°C for several days. Cupric methoxide was prepared according to the method of Brubaker and Wicholas.[6] Cupric acetylacetonate (reagent grade) was recrystallized twice from methanol.[7] Cupric complexes of 1, 10-phenanthroline were prepared *in situ* by dissolving cupric acetate in acetic acid with heat and by then adding a solution of 1, 10-phenanthroline in acetic acid. Care was exercised so as to ensure that the formation of the complexes was complete.[8] Cuprous chloride was prepared according to the method of Keller and Wycoff.[9] The copper contents of these complexes were analyzed iodometrically[10]; the purities of all of them were confirmed to be above 99.2%.

The zinc acetate di-hydrate was of a reagent grade. The zinc chloride was carefully dehydrated *in vacuo*

[*1] Oxidation-Reduction Reactions by Transition Metal Complexes. I.

1) For example, F. Collinson, F. S. Dainton, B. Mile, S. Tazuke and D. R. Smith, *Nature,* **198**, 26 (1963).

2) For example, J. K. Kochi, *Tetrahedron,* **18**, 483 (1962).

3) C. C. Price and E. Krebs, "Organic Syntheses," **23**, 65 (1943).

4) A. I. J. Vogel, *J. Chem. Soc.,* **1948**, 1814.

5) J. F. O'Donnell, J. T. Ayres and C. K. Mann, *Anal. Chem.,* **37**, 1161 (1965).

6) C. H. Brubaker, Jr., and M. Wicholas, *J. Inorg. Nucl. Chem.,* **27**, 59 (1965).

7) R. G. Charles and M. A. Pawlikowski, *J. Phys. Chem.,* **62**, 440 (1958).

8) J. K. Kochi *J. Am. Chem. Soc.,* **84**, 3271 (1962).

9) R. N. Keller and H. D. Wycoff, "Inorganic Syntheses," **2**, 1 (1946).

10) S. Hirano, "Industrial Analytical Chemistry," Kyoritsu, Tokyo (1959), p. 284.

Table 1. Substituted benzoyl peroxides

Benzoyl peroxide	Recryst. solvent	Purity,[*4] %	C% Found	H% Found	N% Found
H-	Chloroform[*1]	99.5	69.40	4.20	—
p-CH_3O-	Toluene[*2]	99.6	63.38	4.65	—
p-NO_2-	Toluene[*3]	99.0	50.87	2.42	8.33

[*1] D. R. Augood, D. H. Hey and G. H. Williams, *J. Chem. Soc.*, **1952**, 2094.

[*2] L. Vanino and E. Uhlfelder, *Ber.*, **37**, 3624 (1904).

[*3] G. Braun, " Organic Syntheses," Coll. Vol. I, p. 431 (1941).

[*4] Analyzed iodometrically, *cf.* A. T. Blomquist and A. J. Buselli, *J. Am. Chem. Soc.*, **73**, 3883 (1951); W. E. Cass, *ibid.*, **68**, 1976 (1946).

with heating it at 110°C for five hours before use. Their zinc contents were not analyzed.

Typical Reaction Procedure. Benzoyl peroxide (6.05 g, 2.50×10^{-2} mol) and cupric acetate (0.908 g, 5.00×10^{-3} mol) were dissolved in 50 m*l* of acetic acid in a three-necked, 100 m*l*, round-bottomed flask equipped with a 30 cm Dimroth condenser, a nitrogen inlet, a thermometer, and a magnetic stirrer. The solution was then swept with oxygen-free nitrogen and heated with stirring at 90.0 ± 1.0°C for 10.0 hr. During the reaction the system was maintained under the nitrogen stream. The volatile reaction products evolved from the top of the condenser were collected in a pair of dry ice-methanol traps. Carbon dioxide was absorbed into a Ascarite tube at the end of the series.

Product Analysis. *For the Reaction in Acetic Acid.* After cooling, the reaction mixture was treated with water, extracted with toluene, washed with a saturated aqueous solution of sodium bicarbonate and then with water, dried on sodium sulfate, and fractionally distilled. This first portion of the distillate (*ca.* 5 m*l*) and the remaining concentrated solution (*ca.* 10 m*l*) were analyzed by g.l.c. employing a 2 m Silicon DC 550 column at 70, 90, and 175°C. Chlorobenzene, bromobenzene, and nitrobenzene were used as markers. The combined aqueous solution was then acidified by concentrated hydrochloric acid, extracted with ether, dried on sodium sulfate, evaporated, and recrystallized from hot water to give a mixture of aromatic carboxylic acids. This mixture was weighed and analyzed by IR spectroscopy.

For the Reaction in Acetonitrile. The reaction mixture was distilled almost to dryness. The remaining solid was treated with ether and filtered. The combined solution from the distillate and the filtrate was fractionally distilled. Analysis by g.l.c. was conducted as in the case of reaction products in acetic acid.

The reproducibilities of the reactions were fairly good.

The products were identified mainly by the retention times of the g.l.c. For the reaction products with cupric bromide and cupric acetylacetonate, however, absorption chromatographic analysis (alumina column: about 300 mesh, $\pi \times 5^2 \times 300$ mm^3, toluene) was carried out. Benzene, bromobenzene, phenyl acetate, biphenyl, and phenyl benzoate were also identified by means of their NMR and IR spectra.

Ultraviolet and Visible Spectra. The ultraviolet and visible spectra were measured on a Hitachi EPS-2 at room temperature, using glass and quartz cells with a path length of 10 mm.

Results and Discussion

Electron Transfer and Ligand Transfer. The results of reactions in acetic acid at 90.0°C are summarized in Table 2. Besides the products listed in this table, appreciable amounts of carbon dioxide and biphenyl were also produced. It should be noted that a remarkable amount of phenyl acetate was produced in the presence of the copper ion. The yield increased considerably with an increase in the initial concentration of the cupric ion. Phenyl acetate was not observed in either the thermal decomposition of benzoyl peroxide in acetic acid11) or in the presence of zinc ion. Furthermore, in the case of cupric propionate, a sizable amount of phenyl propionate was formed. The formation of this "ligand-transfer"12) product, coupled with the observations mentioned above, strongly supports the idea of the oxidation of the phenyl radical by copper(II) complexes.

The presence of molecular oxygen and of hydrated water, however, did not influence the reaction products. Thus, the alternative route for the formation of phenyl acetate *via* the phenylperoxy radical and phenol can not be accepted.

The oxidation mechanisms of organic radicals by transition metal complexes may be classified into two modes; electron-transfer and ligand-transfer.13) For our system, phenyl radical-copper(II) complexes-acetic acid, the schemes may be shown in the following way:

Electron-transfer type:

$$\mathrm{Cu^{II}L_2 + C_6H_5\cdot \rightarrow C_6H_5^+ + Cu^{I}L + L^-} \quad (1)$$

$$\mathrm{C_6H_5^+ + HOAc \rightarrow C_6H_5{-}OAc + H^+} \quad (2a)$$

$$\mathrm{C_6H_5^+ + L^- \rightarrow C_6H_5{-}L} \quad (2b)$$

Ligand-transfer type:

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11) Table 2 and earlier works: M. S. Kharash, E. V. Jensen and W. H. Urry, *J. Org. Chem.*, **10**, 386 (1945); M. T. Gladstone, *J. Am. Chem. Soc.*, **76**, 1581 (1954).

12) Cohen and his coworkers used the terminology "ligand radical transfer." A. H. Lewin, A. H. Dinwoodie and T. Cohen, *Tetrahedron*, **22**, 1527 (1966).

13) J. K. Kochi, *J. Am. Chem. Soc.*, **84**, 774 (1962).

TABLE 2. OXIDATIONS OF PHENYL RADICAL BY COPPER(II) COMPLEXES IN ACETIC ACID
Benzoyl peroxide: 6.06 g (2.50×10^{-2} mol)
Acetic acid: 50.0 ml, 90.0±1.0°C, 10.0 hr

Copper(II)	Complex*1	C_6H_6*1	C_6H_5L*1	C_6H_5OAc*1	C_6H_5OBz*1	Acids*2
——	—	24.4	—	0.00	1.06	0.206
$Cu(OAc)_2$	50.0	32.0	—	6.02	0.10	0.865
$Cu(OAc)_2H_2O$	5.00	23.2	—	3.62	0.00	0.428
$Cu(OAc)_2H_2O$	50.0	35.2	—	7.87	0.00	0.601
$Cu(OAc)_2H_2O$	50.0*3	31.1	—	8.38	0.00	0.698
$Cu(OAc)_2H_2O$	250*4	42.0	—	10.3	0.00	1.713
$Cu(OCOC_2H_5)_2$	50.0	39.4	8.46	3.03	0.00	0.944
$CuCl_2$	50.0	45.8	15.0	2.50	0.00	1.054
$CuBr_2$	50.0	27.0	6.00	2.74	0.00	0.581
$Cu(acac)_2$	50.0	68.2	0.00	35.4	14.4	0.511
$Cu(phen)_1$	50.0*5	51.3	0.00	3.10	0.00	1.463
$Cu(phen)_3$	50.0*5	52.9	0.00	0.30	0.00	1.335
CuCl	50.0	64.2	2.62	1.70	0.00	1.299
$Zn(OAc)_22H_2O$	50.0	24.4	—	0.00	0.00	0.223
$ZnCl_2$	50.0	23.2	1.25	0.00	0.00	0.891

*1 $\times10^4$ mol
*2 $\times10^0$ g
*3 In the presence of molecular oxygen
*4 Inhomogeneous
*5 Prepared *in situ*

$$\mathrm{Cu^{II}L_2} \overset{\mathrm{HOAc}}{\rightleftarrows} \underset{[\mathrm{A}]}{\mathrm{Cu^{II}L(OAc)}} \overset{\mathrm{HOAc}}{\rightleftarrows} \mathrm{Cu^{II}(OAc)_2},\ \textit{etc.} \qquad (3)$$

$$\begin{array}{l} \mathrm{Cu^{II}L(OAc)} \\ \quad + \\ \mathrm{C_6H_5\cdot} \end{array} \left\langle \begin{array}{ll} [\mathrm{CuL\cdots OAc\cdots C_6H_5}] \rightarrow & \\ \qquad \mathrm{C_6H_5\text{-}OAc} + \mathrm{Cu^{I}L} & (4a) \\ [\mathrm{CuOAc\cdots L\cdots C_6H_5}] \rightarrow & \\ \qquad \mathrm{C_6H_5\text{-}L} + \mathrm{Cu^{I}(OAc)} & (4b) \end{array} \right.$$

In the electron-transfer type, the intermediate carbonium ion would react with either the solvent acetic acid or the free ligand anion. Under the conditions employed, the concentration of the free ligand anion is so low that the contribution of the reaction of Eq. (2b) may be considered to be negligible.

For the ligand-transfer reaction, the structure of the oxidant is an essential matter. If, for example, a species such as [A] is formed by the ligand-exchange reaction, two types of products, *i. e.*, phenyl acetate and ligand-substituted benzene, may be expected from a ligand-transfer by this oxidant. Thus, phenyl acetate, the apparent electron-transfer product, may also be produced *via* the ligand-transfer reaction. Since a reaction such as Eq. (3) is a very rapid one,[14] we can assume the inequality below (if, 4a>2b):

True proportion of ligand-transfer

$$\frac{(4a)+(4b)}{(2a)+(2b)+(4a)+(4b)} > \frac{(2b)+(4b)}{(2a)+(2b)+(4a)+(4b)}$$

Apparent proportion of ligand-transfer (5)

The apparent proportion of ligand-transfer for cupric propionate, as calculated from Table 2, is 0.74. Similarly, the large portion of phenyl acetate formed with cupric acetate may also be *via* a ligand-transfer.

The 1 : 3 complex of copper(II)-phenanthroline, despite its higher oxidation potential,[15] produced a much lower yield of phenyl acetate than did the 1 : 1 complex. This phenomenon is most likely attributable to the lack of a coordinative site for acetic acid in the case of the 1 : 3 complex. In other words, it may be highly preferable for the production of phenyl acetate for the acetate ion or acetic acid to reside in the first coordination sphere of the cupric ion. Therefore, we may reasonably presume that, in the oxidation of the phenyl radical by copper(II) complexes, ligand-transfer precedes elctron-transfer.

Additional evidence for this ligand-transfer comes from the reactions in an acetic acid - acetonitrile mixture. These are tabulated in Table 3. With cupric acetate, no solvent dependency of the phenyl acetate yield was observed, showing that the acetate ions in the outer-sphere of the cupric ion do not play a primary role in the oxidation. On the other hand, in the case of cupric acetylacetonate, the yield of phenyl acetate changes considerably with the solvent composition. This result can readily be explained by considering the following equilibrium:

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[14] F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," John Wiley & Sons, New York, N. Y. (1958).

[15] J. K. Kochi, *J. Am. Chem. Soc.*, **84**, 3271 (1962).

TABLE 3. SOLVENT EFFECTS ON THE OXIDATION OF PHENYL RADICAL BY COPPER(II) COMPLEXES
Benzoyl peroxide: 2.42 g (1.00×10^{-2} mol)
Solvent: 50.0 m*l*, 80.0±1.0°C, 10.0 hr

Copper(II)	Complex $\times 10^2$ mol	Solvent	C_6H_5OAc $\times 10^4$ mol
$Cu(OAc)_2$	1.00	HOAc*1	3.16
$Cu(OAc)_2$	1.00	HOAc(20%)-CH_3CN(80%)	7.72
$Cu(OAc)_2$	1.00	CH_3CN	6.10
$Cu(acac)_2$	1.00	HOAc	3.23
$Cu(acac)_2$	1.00	HOAc(20%)-CH_3CN(80%)	0.73
$Cu(acac)_2$	1.00	CH_3CN	—

*1 Inhomogeneous

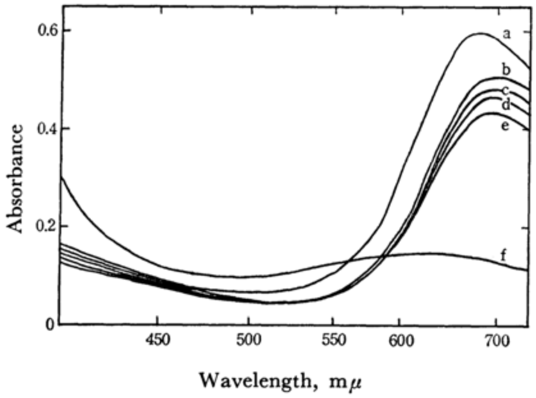

Fig. 1. Absorption spectra of copper(II) complexes in acetic acid and acetonitrile.

a	$Cu(OAc)_2$	2.50×10^{-3} M	HOAc
b	$Cu(acac)_2$	2.50×10^{-3} M	HOAc
c	$Cu(acac)_2$	2.50×10^{-3} M	HOAc(75%)-CH_3CN(25%)
d	$Cu(acac)_2$	2.50×10^{-3} M	HOAc(50%)-CH_3CN(50%)
e	$Cu(acac)_2$	2.50×10^{-3} M	HOAc(25%)-CH_3CN(75%)
f	$Cu(acac)_2$	2.50×10^{-3} M	CH_3CN

$$Cu^{II}(acac)_2 + HOAc \overset{HOAc}{\rightleftarrows} \underset{[B]}{Cu^{II}(acac)_2 \cdot HOAc} \qquad (6)$$

Actually, this was confirmed spectrophotometrically. As is shown in Fig. 1, the concentration of cupric acetate-like species[B] increased with the increase in the acetic acid portion of the solvent mixture. This nicely corresponds to the increase in the yield of the oxidation product.

Oxidation by Copper(II) Halides. Copper(II) halides as oxidizing agents provide some complexity. With these reagents, apart from the above-mentioned mechanisms, the ligand-transfer-type products may also be formed *via* Eqs. (7) and (8):

$$\begin{aligned} &Cu^{II}X_2 + (C_6H_5\text{-}COO)_2 \rightarrow \\ &\qquad Cu^{II}X(C_6H_5\text{-}COO) + C_6H_5COOX \\ &C_6H_5\text{-}COOX \rightarrow C_6H_5\text{-}X + CO_2 \\ &C_6H_5\text{-}COOX + Cu^{II}X(C_6H_5\text{-}COO) \rightarrow \\ &\qquad Cu^{II}(C_6H_5\text{-}COO)_2 + X_2 \end{aligned} \qquad (7)$$

$$C_6H_5\cdot + X_2 \rightarrow C_6H_5\text{-}X + X\cdot$$

$$\begin{aligned} &2Cu^{II}X_2 \rightarrow 2Cu^{I}X + X_2 \\ &(Cu^{II}X_2 \rightarrow Cu^{I}X + X\cdot) \end{aligned} \qquad (8)$$

Reactions of the type of Eq. (7) have been known for lithium halides.[16] It was found in our study that zinc chloride, and probably cupric chloride as well, perform this reaction. Here, however, it must be mentioned that zinc chloride, in spite of its stronger Lewis' acidity,[17] produced a much lower yield of chlorobenzene than did cupric chloride. This fact adequately indicates the minor contribution of the acid-base reaction of Eq. (7) as compared to the oxidation-reduction processes.

It is well known that the thermal decomposition of copper(II) halides proceeds *via* Eq. (8). In certain organic solvents, especially in acetonitrile, copper(II) halides acquire higher oxidation potentials;[18] therefore, the reaction of Eq. (8) becomes much more readily attainable. It results that the yields of halobenzenes are considerably more pronounced in acetonitrile than in acetic acid, as is illustrated in Table 4. The formation of molecular bromine in this system was again confirmed spectroscopically.

TABLE 4. LIGAND TRANSFER REACTION IN ACETONITRILE
Benzoyl peroxide: 2.42 g (1.00×10^{-2} mol)
Solvent: 50.0 m*l*, 80.0±1.0°C, 10.0 hr

Copper(II) CuL_2	Complex $\times 10^3$ mol	Solvent	C_6H_5-L $\times 10^4$ mol
$Cu(OAc)_2$	1.00	CH_3CN	0.44
$Cu(OAc)_2$	10.0	CH_3CN	6.10
$Cu(OCOC_2H_5)_2$	10.0	CH_3CN	6.20
$CuCl_2$	1.00	CH_3CN	7.38
$CuBr_2$	1.00	CH_3CN	8.38
$Cu(OCH_3)_2$	1.00	CH_3CN	13.7
$Cu(OAc)_2$	1.00	HOAc	0.66
$Cu(OAc)_2$	10.0*1	HOAc	3.16
$CuCl_2$	1.00	HOAc	1.02

*1 Inhomogeneous

The Mechanisms of Ligand Transfer. Recent study in our laboratory has revealed that the thermal decomposition of cupric acetate involves

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[16] a) J. K. Kochi, B. M. Graybill and M. Kurtz, *ibid.*, **86**, 5257 (1964); b) J. K. Kochi and R. V. Subramanian, *ibid.*, **87**, 1508 (1965).

[17] G. A. Olah, "Friedel-Crafts and Related Reactions," Vol. I, Interscience Publishers, New York, N. Y. (1963), p. 858.

a one-electron transfer from the ligand to the central metal atom.[18] This is just that of the reaction of Eq. (8), and provides a probable mechanism for ligand-transfer. However, an alternative mechanism involving the incipient carbonium ion intermediate is also probable:

Radical mechanism:

$$\mathrm{Cu^{II}L_2 + C_6H_5\cdot \rightarrow [Cu^{I}L\cdots\dot{L}\cdots C_6H_5\cdot] \rightarrow Cu^{I}L + C_6H_5\text{-}L} \qquad (9)$$

Incipient carbonium ion mechanism:

$$\mathrm{Cu^{II}L_2 + C_6H_5\cdot \rightarrow [Cu^{I}L_2{}^{-}\cdots C_6H_5{}^{+}] \rightarrow Cu^{I}L + C_6H_5\text{-}L} \qquad (10)$$

The effects of substituents on the oxidation of the phenyl radical by cupric acetate in acetonitrile were also examined. It may be seen from Table 5 that the introduction of an electron-donating group on the benzene nucleus enhances the oxidation. However, the effects are so small that one can hardly distinguish between the mechanism of Eq. (9) and that of Eq. (10).

TABLE 5. OXIDATIONS OF SUBSTITUTED PHENYL RADICALS
$\mathrm{Cu(OAc)_2}$ 1.82 g (1.00×10^{-2} mol)
$\mathrm{CH_3CN}$ 50.0 m*l*, 80.0±1.0°C, 10.0 hr

(p-Y-$\mathrm{C_6H_4COO)_2}$	g	$\times10^2$ mol	p-Y-$\mathrm{C_6H_4OAc}$ $\times10^4$ mol
(p-$\mathrm{CH_3O}$-$\mathrm{C_6H_4COO)_2}$	3.02	1.00	6.25
$\mathrm{(C_6H_5COO)_2}$	2.42	1.00	6.10
(p-$\mathrm{NO_2}$-$\mathrm{C_6H_4COO)_2}$	3.32	1.00	5.91

The Behavior of Copper(I) Complexes. With cuprous chloride, in separated runs, an appreciable amount of chlorobenzene was obtained. The oxidizing species in these cases were probably produced from Eqs. (11),[19] (12),[20] and (13):

$$\mathrm{Cu^{I}L + (C_6H_5\text{-}COO)_2 \rightarrow \underset{[C]}{Cu^{II}L(C_6H_5\text{-}COO)} + C_6H_5\text{-}COO\cdot} \qquad (11)$$

$$\mathrm{Cu^{I}L + C_6H_5\text{-}COO\cdot \rightarrow Cu^{II}L(C_6H_5\text{-}COO)} \qquad (12)$$

$$\mathrm{Cu^{I}L + C_6H_5\cdot + HOAc \rightarrow Cu^{II}L(OAc) + C_6H_6} \qquad (13)$$

The remarkable yields of carboxylic acids and benzene in the presence of the copper ion are consistent with this view. The reaction of Eq.(11) was shown to be very fast.[19] Hence, it appears plausible to assume that the steady-state concentration of the cuprous ion is negligible compared to that of the cupric ion during the course of the reaction.

The oxidation reaction by the species [B] may be similar to that of the species [C]. As may be seen from Table 3, the sequence of the ease of ligand-transfer is as follows:

Halides > Carboxylates ≫ Acetylacetonate. Thus, if L is a halide, the production of halobenzene prevails, whereas if L is an acetylacetonate, the production of phenyl benzoate may be expected. This is just the case, as Tables 2 and 3 show.

Further studies are under consideration, especially that of the abnormally great efficiency of cupric acetylacetonate in the production of phenyl acetate, biphenyl, and phenyl benzoate.

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18) To be published.

19) J. K. Kochi, *J. Am. Chem. Soc.*, **84**, 1572 (1962).

20) A. L. J. Beckwith and G. W. Evans, *Proc. Chem. Soc.*, 63 (1962).